

ISOTHERMAL CRYSTALLIZATION MEASUREMENTS ON COPOLY-ESTERS BY DIFFERENTIAL SCANNING CALORIMETRY

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Miller's method for isothermal crystallization measurement was used to determine the progress of crystallization of copoly(ethylene terephthalate/isophthalate) and copoly(ethylene terephthalate/5-methoxyisophthalate) by DSC. The evaluation of kinetic parameters is too complicated for higher contents of comonomer and higher values of molecular mass of copolyesters. On the other hand, the experimental results interpreted by the simplified equation well characterized the differences in the rates of crystallization of different copolyesters.

Some changes of physical properties of polymers during the transition from an amorphous state to a crystalline one have been used for kinetic investigations of crystallization. The classical methods employ measurement of volume or density changes of a polymer. Kolb and Izard [1] first measured the density changes of poly(ethylene terephthalate) (*PET*), while Rybníkář [2] used dilatometry for kinetic measurements. Crystallization measurements can also be investigated in this way when annealed *PET* samples are cooled below the glass transition temperature (T_g) in various time intervals and the density is then measured in a gradient column [3]. As regards measurement of density changes, there are some exceptions to this method since the density of non-crystalline regions can vary [4]. As non-oriented polymers crystallize in the form of spherulites, the progress of crystallization can be determined by measuring the rate of spherulites growth [5, 6]. Crystalline formations show some birefringence and this fact is used for perceiving the changes of light polarization during the crystallization process [7, 9]. Furthermore, infrared spectroscopy has been used for this purpose [10].

Even differential scanning calorimetry (DSC) is generally suitable for isothermal crystallization measurements, though its employment is not conventional in this sphere [11, 12]. Differential thermal analysis is not applicable at all [13]. This is evidently connected with the fact that DSC is not very suitable for isothermal measurements. For example, stabilization of the required isothermal temperature lasts 2 minutes, using a Perkin-Elmer DSC-1B. Classical calorimetry is more advantageous for isothermal measurements [14].

Miller's method [15] is the only one using DSC for isothermal crystallization measurements on *PET*. This method enables one to measure a rate of *PET* isothermal crystallization in the range from 100 to 115°. Thus, the sample is annealed

for a varying time period at constant temperature and then the change in area of the cold crystallization peak is observed during the successive heating. In our work, too, this method has been used for the determination of the progress of crystallization of copolyesters.

Experimental

Copolyesters were prepared by transesterification of dimethylterephthalate and dimethylisophthalate or dimethyl-5-methoxyisophthalate with ethylene glycol and by successive polycondensation in the melt at 280° and under a pressure of 113 Pa. $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2 \text{H}_2\text{O}$ (0.025 mole %) and $\text{Sb}(\text{CH}_3\text{COO})_3$ (0.036 mole %) were used as catalysts. H_3PO_4 (0.03 mole %) was used as stabilizer.

The list of polyesters used, as well as intrinsic viscosity values are given in Table 1.

Table 1

The samples of polyesters used and their crystallization data at the crystallization temperature 109.7°

Sample	Kind of copolyester	$[\eta]^{\times\times}$, ml/g	Half-time of crystallization, $t_{1/2}$ min	Rate constant $k \times 10^3 \text{ min}^{-1}$
1	unmodified <i>PET</i>	75.0	122.0	5.7
2	unmodified <i>PET</i>	65.2	29.5	23.5
3	3 mole % <i>EM</i> ***	70.0	374.0	1.9
4	3 mole % <i>EM</i>	54.8	274.7	1.9
5	5 mole % <i>EM</i>	67.2	—*	—
6	8 mole % <i>EM</i>	54.8	—	—
7	8 mole % <i>EM</i>	69.2	385.1	1.8
8	8 mole % <i>EI</i> **	72.8	—	—
9	8 mole % <i>EI</i>	57.2	207.9	3.3

Notes: * The relationship is non-linear in Fig. 4, and hence $t_{1/2}$ and k cannot be calculated

** *EI* — ethyleneisophthalic structural units

*** *EM* — ethylene-5-methoxyisophthalic structural units

×× Intrinsic viscosity $[\eta]$ was determined from the extrapolation of reduced viscosity $\eta_{\text{red}} = (\eta_{\text{rel}} - 1/c)$ of copolyester at five concentrations to infinite dilution. Relative viscosity η_{rel} was measured in the mixture of phenol-tetrachloroethane (1 : 3) at 30°.

After extrusion, the copolyester melt from a laboratory polycondensation equipment was quenched in the form of a foil. A sample was inserted into a sample pan and closed. The weight of a sample was 8–12 mg. A Perkin-Elmer DSC-1B was used for the measurement.

Miller's method [15] is based on the following assumptions: if the amorphous polyester is heated from a temperature lower than T_g , an exothermic peak of cold

crystallization appears on the trace in the region above this temperature. On the other hand, if isothermal annealing is performed at a temperature higher than T_g but lower than the mentioned temperature of the exothermic peak, then the area of the exothermic peak is smaller. The difference between the two exothermic peak areas is proportional to the crystalline part formed by isothermal crystallization at the temperature of annealing (Fig. 1).

The temperature 109.7° was established for isothermal crystallization of amorphous copolyesters. A series of 5–7 samples was prepared and these were annealed at the said temperature for different time periods. The first sample was not annealed ($t = 0$ min). The subsequent time intervals were chosen tentatively according to

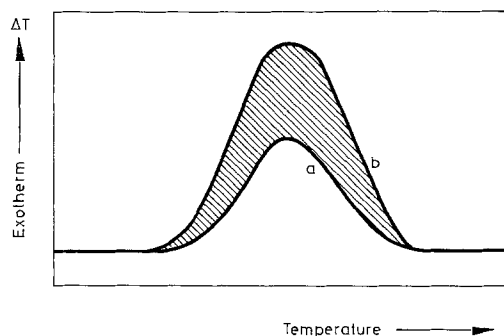


Fig. 1. DSC curve taken according to Miller's method [15] of isothermal crystallization measurements. The hatched area is proportional to the heat released during isothermal crystallization. a, peak of cold crystallization after annealing; b, peak of cold crystallization of amorphous sample

the rate of crystallization of the given sample. The heating rate was 16 K/min, and the ordinate sensitivity was 33.5×10^{-6} Js $^{-1}$ full scale. The areas of cold crystallization peaks were measured with a planimeter. The enthalpy of cold crystallization was calculated from the sample weight and the calibration constant. The difference between the enthalpies of an original sample and a sample crystallized at 109.7° for a time t is proportional to the crystalline part formed during isothermal crystallization at 109.7° . In some cases the temperature of the maximum of the exothermic peak (T_c) was read from the chart.

Results and discussion

The total rate of crystallization can be described by the empirical Avrami's equation

$$1 - \Theta = \exp(-kt^n) \quad (1)$$

where: Θ = the crystalline part of polymer

k = rate constant

n = Avrami's exponent

The crystallization rate is to be characterized either by a rate constant k which does not consider the influence of nucleation, or by a crystallization half-time ($t_{1/2}$) according to [16]

$$(t_{1/2} = (\ln 2/k)^{1/n} \quad (2)$$

Mayhan et al. [17] calculated the rate constant and the crystallization half-time according to the functions

$$\ln(1 - \Theta) = -kt; \quad (3)$$

$$t_{1/2} = \ln 2/k$$

using $n = 1$, seeing that $n = 1.14$ at 110.0° according to their measurements [17].

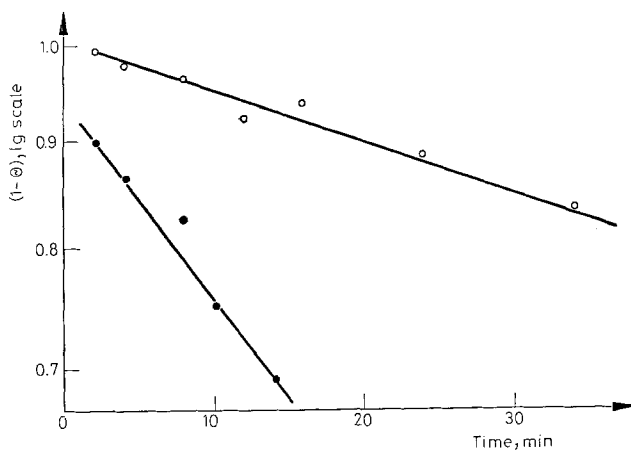


Fig. 2. Logarithm of non-crystalline fraction as a function of time for two samples of *PET* with different molecular weights. ●: $[\eta] = 0.62$; ○: $[\eta] = 0.750$

Figure 2 includes the kinetic data of *PET* samples with various molecular weights (characterized by $[\eta]$). A function of $\ln(1-\Theta)$ against t is linear and a higher crystallization rate is to be observed at lower molecular weight. It is also possible to use the maximum of the crystallization peak (T_c) for relative estimation of the crystallization rate.

The relation between molecular weight and T_c is shown in Fig. 3. This relative comparison is to be used for the samples of an identical polymer. There is a little more complicated situation for copolyesters. The course of the crystallization is shown in Fig. 4. In this case, no unambiguous relation was found, such as the temperature T_c increasing with decreasing crystallization rate under isothermal conditions at 109.7° .

This phenomenon can be explained in the following way: Any variation in molecular weight conduces to a variation of crystallization rate at all temperatures.

On the other hand, the temperature of the minimum crystallization half-time ($t_{1/2}$), which is situated between T_g and the melting temperature T_m , remains constant. In the case of copolymers, both T_g and T_m are changed in comparison with the homopolymer. Consequently, the temperature of minimum $t_{1/2}$ is changed, too.

Kinetic data on crystallization of various copolyesters are given in Fig. 4. They are copoly(ethylene terephthalate/isophthalate) and copoly(ethylene terephthalate/methoxyisophthalate). As is clear from both Fig. 4 and Table 1, the relations [3] cannot be used for evaluation of kinetic data when both the content of the modifying component and the molecular weight are higher. The relations are not

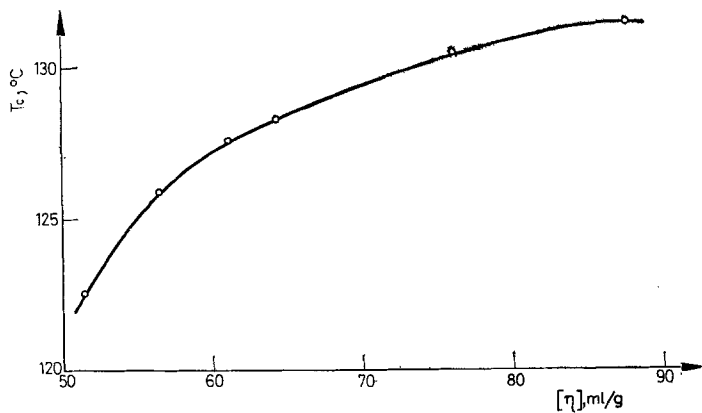


Fig. 3. T_c vs. the intrinsic viscosity of PET.

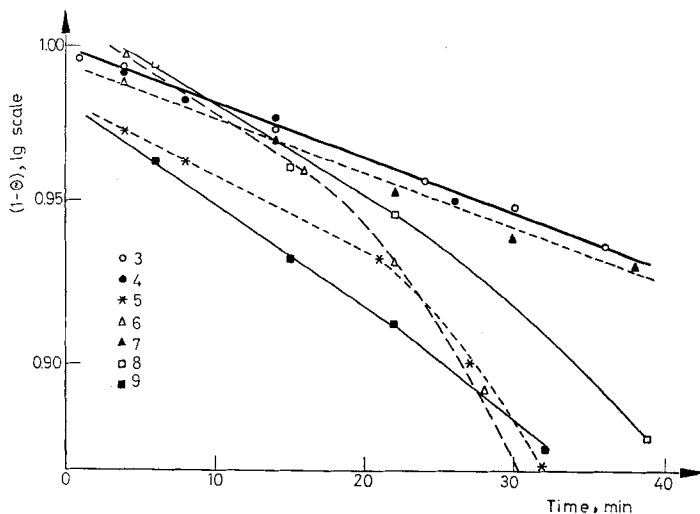


Fig. 4. Logarithm of non-crystalline fraction as a function of time for copolyesters.

linear in such cases. It would be necessary to use more general equations than (1) and (2).

Our experiments show that Miller's method [15] is applicable to many different polyesters. Nevertheless, the half-times calculated for *PET* from Fig. 2 are greater than those calculated by Miller. This may be connected with the value used for the *PET* molecular weight. There is probably some difference in calculation. In our case, the peak of cold crystallization represents an exothermic reaction with a thermal effect of about 40 J/g. This value represents about 30% crystallinity. The same value was obtained by Miller [15]. He related the degree of crystallinity of *PET* to this value (40 J/g). In our case we related the degree of crystallinity to the 100% crystalline polymer, and this represents about 120 J/g according to the literature data. We preferred this way because we cannot assume that the peak area of the cold crystallization corresponds to the ultimate crystallinity of a polymer in the investigated temperature range. The peak areas of the cold crystallization of copolyesters are smaller than that for *PET*. This would necessitate the rate of crystallization of copolyesters related to lower base being even higher than that of *PET*. Such findings do not agree with those of other methods.

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RÉSUMÉ — On a appliqué la méthode de détermination de la cristallisation isotherme de Miller à la détermination par analyse calorimétrique différentielle de l'avancement de la cristallisation du copoly(éthylène téréphtalate/isophtalate) ainsi que du copoly(éthylène téréphtalate/5-méthoxy-isophtalate). L'évaluation des paramètres cinétiques est trop compliquée pour les teneurs plus élevées en comonomère et pour les valeurs plus élevées de la masse molaire des copolyesters. D'autre part, les résultats d'expériences interprétés par l'équation simplifiée ont bien caractérisé les différences de vitesses de cristallisation des divers copolyesters.

ZUSAMMENFASSUNG — Die Millersche Methode der isothermen Kristallisierung wurde eingesetzt um den Fortschritt der Kristallisierung von Kopoly(Äthylen-Terephthalat/Isophthalat) und Kopoly(Äthylen-terephthalat/5-Metoxisophthalat) mittels DSC zu untersuchen. Die Auswertung der kinetischen Parameter ist für höhere Ko-Monomergehalte und höhere Molekularmassenwerte der Ko-Polyester zu kompliziert. Andererseits konnten die an Hand der vereinfachten Gleichung gedeuteten Versuchsergebnisse zur Charakterisierung der Unterschiede der Kristallisierungsgeschwindigkeiten der verschiedenen Ko-Polyester mit gutem Erfolg eingesetzt werden.

Резюме — Метод Миллера для измерения изотермической кристаллизации был использован в ДСК для определения развития кристаллизации кополимера этилентерефталат-изофталат и кополимера этилентерефталат-5-метоксиизофталат. Выделение кинетических параметров является слишком сложным для более высокого содержания комономера и более высоких значений молекулярной массы кополиэфиров. С другой стороны, экспериментальные результаты интерпретированы на основе упрощенного уравнения, которое хорошо характеризует различия в скорости кристаллизации различных кополиэфиров.